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PROCEEDINGS

Microbial Degradation of Polymeric Materials

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ABSTRACT

Microorganisms and their products may be responsible for changes in physical, chemical, and electrochemical properties of polymeric materials. We investigated microbial degradation of polyimides used as insulators in electronic packaging. Growth of microorganisms on these polymers was found to result in loss of their dielectric properties. Failure of polyimide films on stainless steel coupons caused by microbial degradation was evaluated with a fungal consortium partially identified as *Aspergillus versicolor*. We obtained distinctive electrochemical impedance spectroscopy (EIS) spectra showing failed polyimides in the presence of the fungal consortium. Decrease of film resistance by two orders of magnitude relative to uninoculated control systems was observed within one week of incubation. The relationship between changes of impedance spectra and microbial degradation of the coatings

was further established by scanning electron microscopic (SEM) observations of fungi on the surface of the polyimides.

We also studied the biodeterioration of fiber reinforced composites, graphite sheets, and graphite fibers used in composite materials. One set of samples was inoculated with the fungal consortium mentioned above, and another set was kept sterile. In all inoculated treatments the fungi adhered to and grew on the composites, graphite sheets, and fiber surfaces. SEM was used to determine adhesion of fungi and subsequent etching of the samples. Fungal penetration into composite resin and graphite sheets was observed. Our data indicate that fungi may cause substantial damage to composites under conditions favorable to fungal growth.

INTRODUCTION

Polyimides are an important class of electronic packaging materials used in fabrication of integrated circuits (Lai, 1989). They are also being utilized in the manufacture of new high-temperature resistant composites. Fiber reinforced composites (FRC) have wide applications in transportation, aviation, and aerospace (Delmonte, 1981). Recently, a new process of thermosetting composites using polyimides has been developed because of the high temperature resistance of this polymer. Further development of high strength, stiffness, and lower weight FRC's compared to alloys has been accelerated due to the corrosion resistance of this class of engineered materials.

Composites have a two-phase structure: a fiber which acts as the reinforcement, and a resin matrix which bonds and holds all the fibers. A maximum number of fibers is contained per unit volume as a means of increasing the strength of the composite material since the fiber dictates the strength, and each fiber takes its full share of the load. The structural integrity of the composite material is the key to its performance success.

A number of factors may influence the integrity of a FRC, including bonding between fiber and matrix, distribution and orientation of fibers in the matrix, and responses of each composite constituent to environmental conditions including moisture, temperature, and microbial contamination. Weakening of one composite constituent can cause progressive delamination, disbonding and separation of the fibers from reinforcing

resin matrices, resulting in reduced strength and stiffness. Failure initiation factors include imperfections, weakening of the interface bonding between the fibers and matrix, and further delamination and separation of the two components (Agarwal and Broutman, 1990). In a study of the corrosion of graphite fibers/magnesium alloy composites in a very dilute NaCl solution, Trzaskoma (1986) reported that severe degradation of graphite fibers was observed after a five-day exposure period.

It is suspected that biological damage to a composite material may significantly affect its physical integrity and fatigue performance. Since there are several chemically and physically distinguishable constituents in a composite, localized chemical changes resulting from growth and metabolism of microorganisms may accelerate damage to composite constituents. Specific surfaces or voids in the FRC may concentrate nutrients, providing a favorable microenvironment for microbial development. Fibers may serve as capillaries to improve the movement and distribution of moisture and chemical species within the composite, and may enhance the spread of microorganisms within the composite structure. Slight chemical changes in localized regions may drastically decrease the material's performance and weaken the composite's physical properties. Knowledge of the effect of microorganisms on the integrity of composite materials is needed for a comprehensive assessment of microbial damage and for the future development of resistant materials.

This report describes preliminary studies of microbial degradation of polyimides and composites by a fungal consortium under laboratory conditions. Electrochemical impedance spectroscopy (EIS) was used to measure polyimide coating deterioration in electrochemical cells.

MATERIALS AND METHODS

Electrochemical impedance spectroscopy (EIS): EIS cells were constructed by gluing a 50.0 mm long acrylic tube (30.0 mm diameter and 4.0 mm thickness of the wall) onto a steel coupon (50.0 X 50.0 mm) by epoxy (Devcon 5 minute Epoxy, Danver, MA 01923). The steel coupons were previously attached with a round piece of Kapton polyimide film as received from Du Pont Co. The adhering material for the film onto the coupon was silver epoxy (SPI Instrumental, West, PA). After drying, 15.0

mL of 0.2 *M* NaCl solution were added into the acrylic tube to serve as working electrode during determination. A diagram of the cell is shown below.

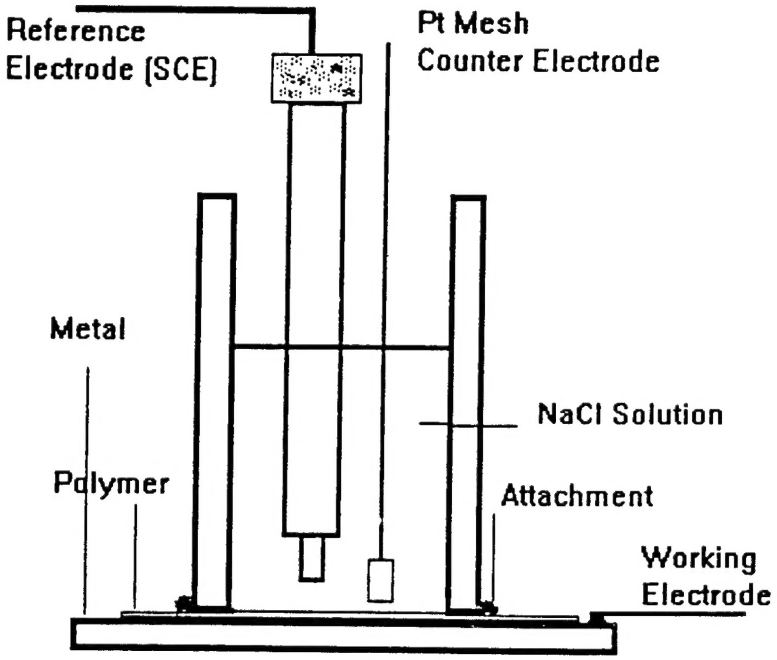

Figure 1. Schematic diagram of the electrochemical cell used

Our EIS consists of a Schlumberger 1250 frequency response analyzer with Schlumberger 1286 electrochemical interface. During data acquisition, samples were potentiostatically held at their open circuit potential (OCP) and a sinusoidal perturbation of 20-50 mV applied to the system. The impedance response was measured over a range of frequencies from 65 kHz to 1 mHz and spectra were recorded as a function of immersion time at ambient temperature. OCP were monitored versus a saturated calomel electrode. The electrode was polarized to its OCP and an AC signal of 20 mV superimposed. Frequency were swept from 65 KHz to 1 mHz and the gain and phase shift monitored. Both Bode plots were used to provide information on increases in porosity, local defects and delamination (Titz et al., 1990)

At weekly intervals, EIS cells of inoculated and sterile control coupons were determined on EIS for their impedance responses. When film failure was observed, film in the EIS cell was taken and prepared for examination by scanning electron microscopy (SEM).

SEM sample preparation: Samples of polyimide films, graphite sheets, fibers and composite material were prepared for SEM examination as follows: samples were treated with 3% glutaraldehyde buffered with 0.2 *M* sodium cacodylate in deinonized water filtered through 0.2 μm polycarbonate membrane filter (Gelman Science, Ann Arbor, MI), washed with 0.2 *M* Na cacodylate three times, fixed in 1% osmium tetraoxide with 0.1 *M* Na cacodylate, and rinsed with Na cacodylate and deionized water. Dehydration of samples was accomplished in an ethanol-distilled water series of 40 to 80% ethanol with increments of 10%, and 85 to 100% ethanol with 5% increments. Samples were then critical point dried in liquid CO_2 (Samdri PVT-3B, Tousimis Research Co., Rockville, MD), coated with platinum and viewed under an AMR 1000 SEM.

Incubation studies: Composites (labeled from A to E), graphite sheets (Goodfellow Co., Malvern, PA), and graphite fibers (P-25, P-100, and Toray), were autoclaved before aseptic introduction into culture flasks containing 80 mL of Malt Broth medium (Difco Lab., Detroit, MI). One set of flasks was inoculated with the above mentioned fungal consortium and another set was kept sterile. At monthly intervals, samples from the inoculated and control flasks were taken for SEM examination.

RESULTS AND DISCUSSION

Biodegradation of Polyimides

Polyimide degradation was observed on the inoculated EIS cells within the first week of incubation (Fig. 2a). During the same period of time, there were no apparent changes in the sterile cells (Fig. 2b). EIS measures the resistive, capacitive, and inductive components of the overall interfacial impedance. Resistance of the polyimide films dropped from 10^8 to about 10^6 Ohms cm^{-2} within the first week. A coating resistance of 10^7 Ohms cm^{-2} is considered "good." Such a large decrease in resistance reflects significant microbially caused changes in the coating dielectric properties. These results suggest that EIS is a particularly useful analytical technique to carry out accelerated testing of microbial deterioration of coating materials.

Over the one week incubation, there was increased permeability of the polyimide coated metal indicating the failure of protective properties of the polyimide exposed to the fungi. Association of fungi with the

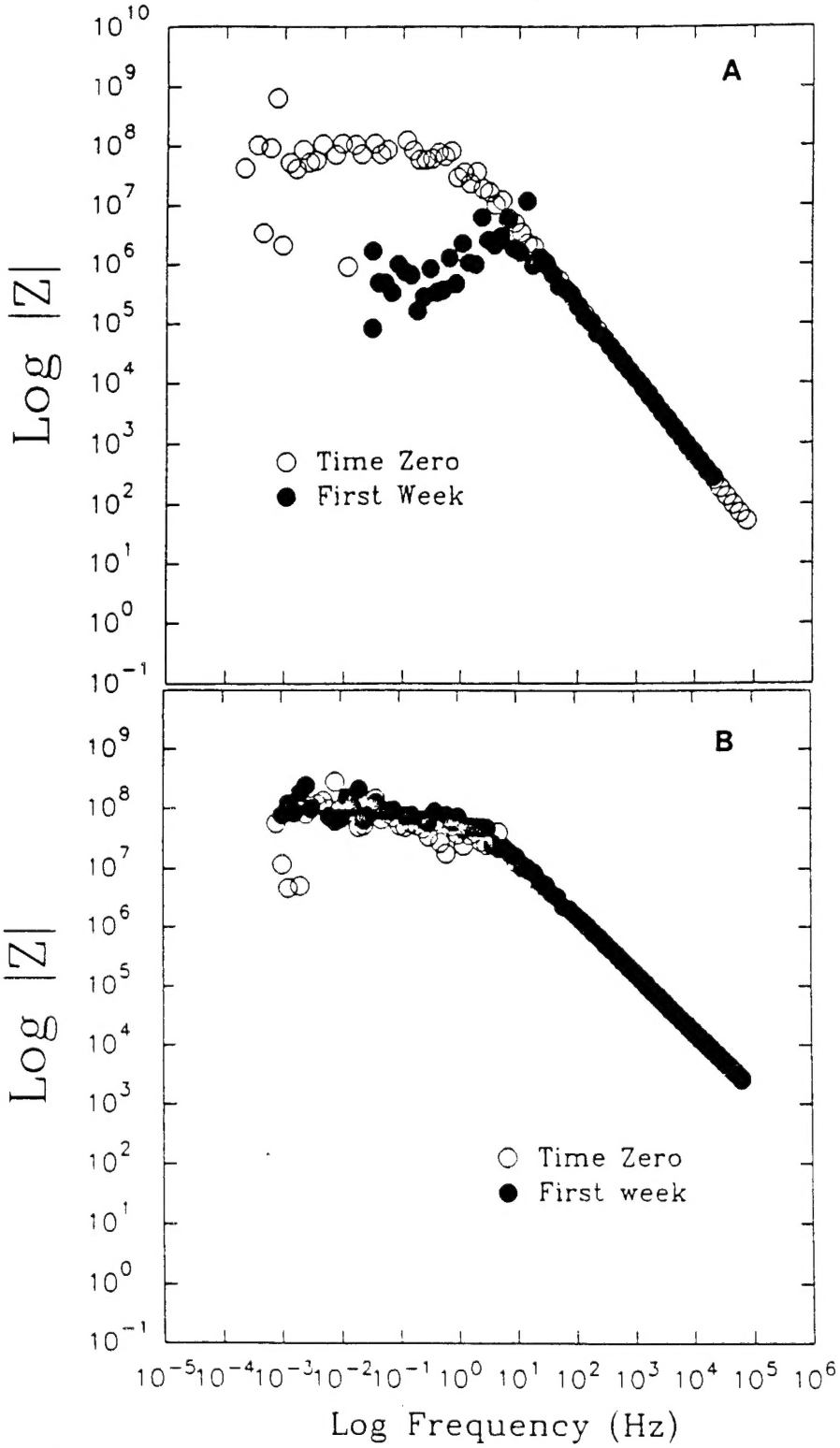

Figure 2. Bode plots of EIS cells inoculated with fungal consortium (A) compared to the sterile control (B)

polyimide failure was observed by SEM examination of the deteriorated film (Fig. 3). Fungi were found to be associated with the degradation of polyimide coating and the deterioration of coating dielectric properties. Though it is not conclusive at this stage if the fungi utilize polyimides as a source of carbon and energy, further studies will provide information on the mechanism by which polyimide coatings are degraded.

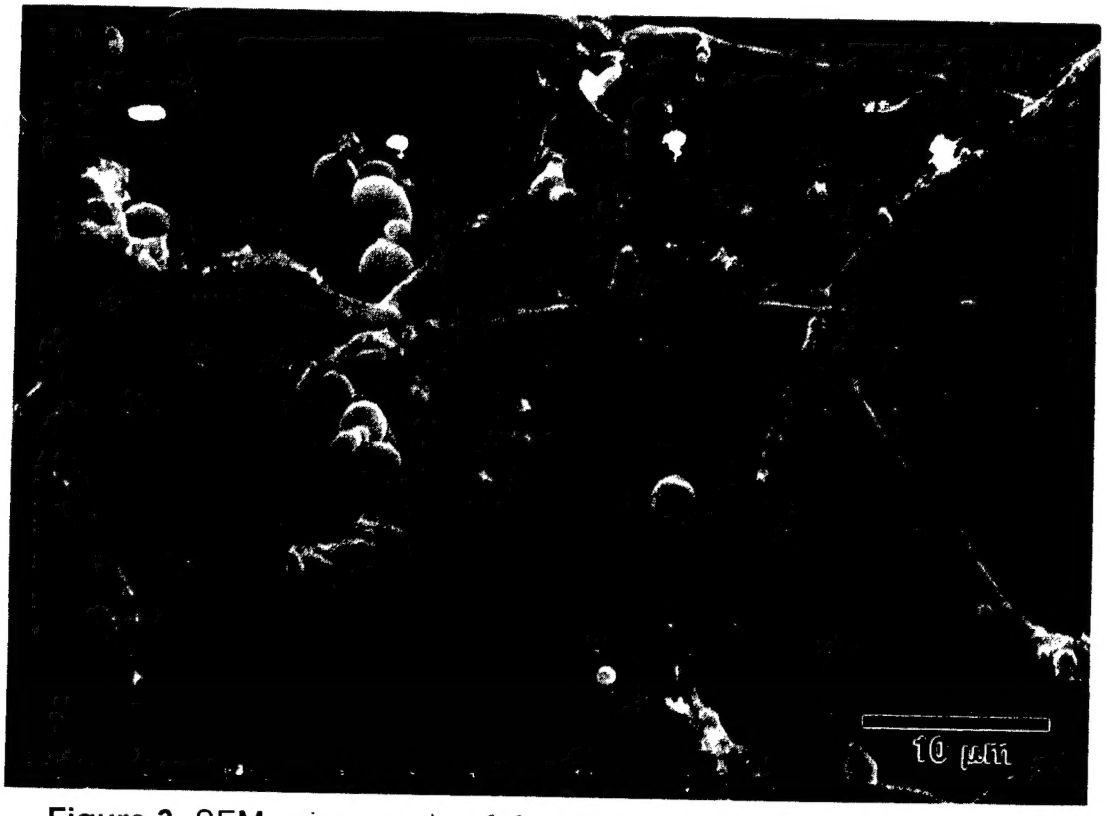

Figure 3. SEM micrograph of fungi on deteriorated polyimide films from an inoculated EIS cell after 7 days of inoculation

Susceptibility of fiber reinforced composites to fungi

We examined five composites for their susceptibility to degradation by our fungal consortium. Effects of fungal degradation on composite mechanical property are reported separately (Thorp et al., 1994). Results suggest that the composite (sample A) containing AFR-700 resin was the most susceptible to fungal attack. Localized penetration of composite resins by fungal hyphae was shown by SEM (Fig. 4). The stability of the resin is important to the performance of the complex composite materials.

Impurities can catalyze the breakdown and directly accelerate the degradation of the composite (Wilkins et al., 1982).

Figure 4. SEM micrograph of fungi on the composite containing AFR-700 resin after 30 days of incubation

These preliminary results prompted us to test the polymer constituents by incubating graphite sheets and graphite fibers (P-25, P-100, and Toray) with the same fungal consortium under the same conditions. Our results on these materials showed that fungi have the ability to colonize the surface of both graphite sheets and fibers extensively. Fungal penetration into graphite sheets was observed (Fig. 5). On day 84 P-100 fibers were found to be covered with fungal hyphae (Fig. 6). It appears that fibers in the composite promote fungal colonization by serving as capillaries for transporting chemicals from susceptible regions or external surfaces, stimulating extensive microbiological invasion and colonization of the composite materials.

Christner et al. (1987) suggested that material degradation advances by crack propagation. In acid environments, degradation occurs along crack lines. Microcracks in the composites are a result of

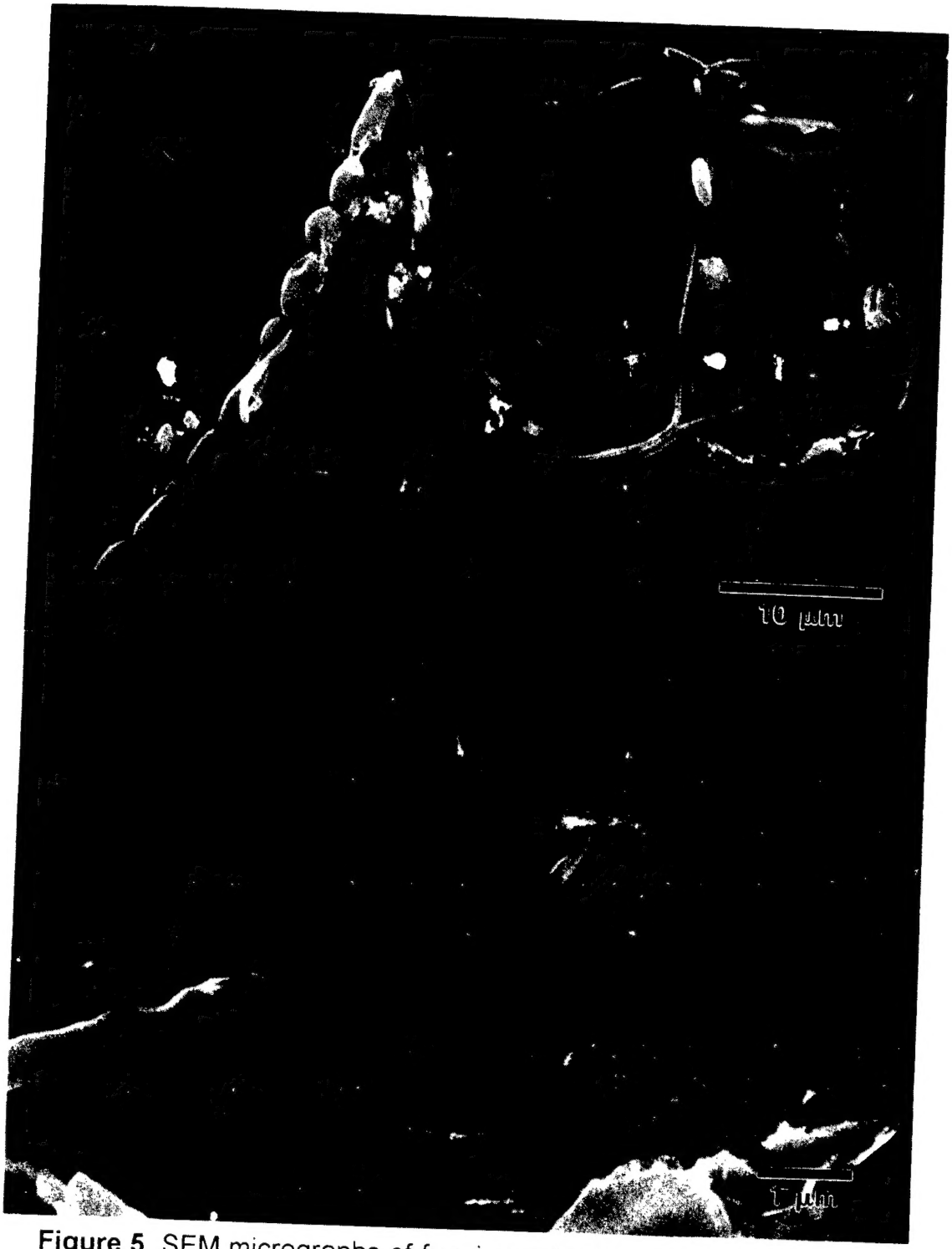

Figure 5. SEM micrographs of fungi penetrating a graphite sheet after 30 days of incubation

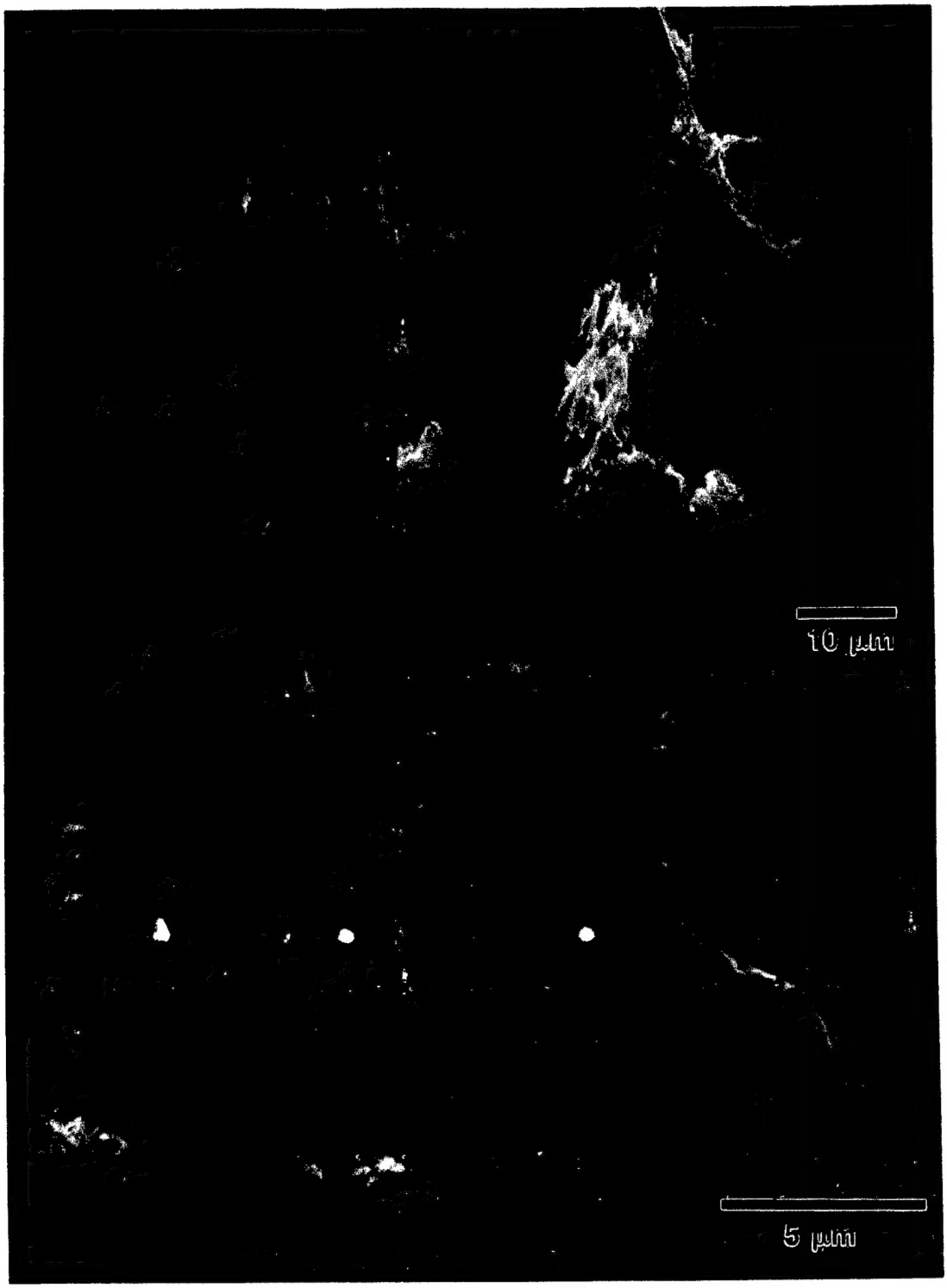

Figure 6. SEM micrographs of fungi growing on graphite fiber P-100 on day 84 of incubation

the curing process in which the resin becomes hard while forming a close association with the fibers embedded in it. Commonly used resins are polyesters, epoxies and phenolics which hold the fibers in position and serve as the matrix material. Epoxy or polyester resins can absorb up to 4-5% by weight of water when exposed to humid conditions (Agarwal and Broutman, 1990). However, the water is not evenly distributed in the resin matrix, but in micropores and microcracks that are sufficiently large for the colonization of microorganisms. The success or failure of FRCs is also governed by the degree of adhesion occurring between the fiber surface and the resin matrix.

It is standard practice to coat the surface of the filaments with a sizing chemical to provide a better bonding with the resin matrix and to prevent abrasion between individual fibers during shipping and handling This treatment permits optimal stress transmission between filaments. The fiber sizing is often a starch-oil mixture used to minimize the degradation of strength resulting from abrasion between fibers, and as a coupling agent to the matrix. The sizing materials are highly susceptible to biodegradation and can be expected to decompose in the presence of contaminating microorganisms

Biodeterioration of graphite sheets by our fungal consortium was also studied. However, it is not clear from this study to what degree graphite fibers may be degraded. The answer to this question requires more sophisticated studies using surface analytical techniques.

Further testing of resins and sizes will enable us to identify the susceptible constituents of composites and the extent of the damage to composite materials. In addition, application of surface characterization techniques should improve our understanding of the mechanism of microbial deterioration of the composites.

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